

OXIDATIVE RANCIDITY AND THE USE OF ANTIOXIDANTS

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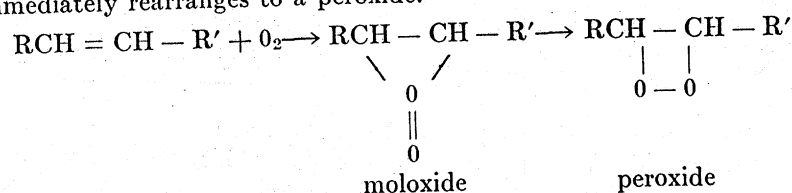
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DIFFERENT TYPES OF FAT SPOILAGE have been discussed in the literature under the general term "rancidity." The type caused by atmospheric oxidation is considered to be responsible for the greatest economic losses in commercial fats and fatty foods.

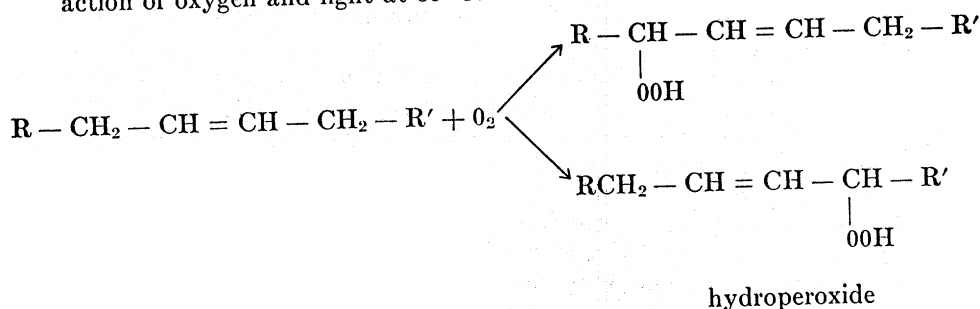
It is well known that many organic compounds and substances other than fats undergo air oxidation and even form the same general type of primary oxidation product, namely, a peroxide. Since a catalyst or an inhibitor of oxidation effective for one type of organic substance is often effective for other organic compounds, the mechanism and control of atmospheric oxidation are of widespread interest and importance.

Oxidation of Fats

Although the first or primary product of air oxidation of fats is peroxidic, there is some question about the structure of the peroxide and the point of attack of the oxygen in the carbon chain. Staudinger (17) postulated that a moloxide first forms at the double bond and then immediately rearranges to a peroxide.



Farmer, *et al.* (5), however, found that a hydroperoxide was formed at the C— atoms adjacent to the double bond of methyl oleate by the action of oxygen and light at 35°C.



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Natural fats present a more complicated picture in respect to peroxide formation and rancidification, since they contain substantial amounts of polyunsaturated acids in addition to oleic acid. Bergström (1) presented evidence indicating that the primary product of oxidation of linoleic acid with molecular oxygen is also a monohydroperoxide formed at the active methylene group (C_{11}) between the double bonds. This hydroperoxide rearranges rapidly to a mixture of 9-hydroperoxido, 10, 12-octadecadienoic and 13-hydroperoxido, 9,11-octadecadienoic acids. These polyunsaturated acids oxidize many times faster than oleic acid, as shown by the data in Table I. The level of oxygen absorption at

TABLE I
OXYGEN ABSORPTION OF METHYL ESTERS OF FATTY ACIDS AT 100° C (18)

SUBSTRATE		OXYGEN ABSORPTION	
% Methyl Esters	Iodine Number	Minutes Required to Absorb 1g./kg.	Grams per Kilogram Absorbed at 60 Minutes
100 Linolenate	260.4	7	19.1
100 Linoleate	172.4	11	10.2
90 Linoleate, 10 Stearate	155.2	13	10.0
80 Linoleate, 20 Oleate	155.0	15	8.4
50 Linoleate, 50 Oleate	129.0	17	6.6
50 Linoleate, 50 Stearate	86.2	18	5.0
25 Linoleate, 75 Stearate	43.1	35	2.6
20 Linoleate, 80 Oleate	103.0	36	2.9
100 Oleate	85.6	115	.2
85 Oleate, 15 Stearate	72.8	166	.2
57 Oleate, 43 Stearate	48.8	337	.1
100 Stearate	0	1250	.05

which the comparative values were obtained corresponds approximately to the "rancidity end-point" ordinarily used in stability tests. It is apparent that in the mixtures containing methyl linoleate and methyl oleate, the latter absorbed little if any oxygen during the pre-rancid stage, indicating that the polyunsaturated acids are primarily responsible for rancidity in fats and oils. The data, however, do not preclude the possibility that the peroxides of linoleic ester or glyceride may react with oleates to produce rancid products.

Fat peroxides are presumed to decompose or undergo further oxidation and cleavage, forming volatile rancid products. Undoubtedly, rancid fat owes its objectionable odor and flavor to more than one oxidation product. Of the products that have been isolated, low molecular weight aldehydes, ketones, and acids, up to 9 C— atoms in chain length, are thought to be the chief offenders, although the possibility that volatile per-acids are formed by further air oxidation of the aldehydes should not be overlooked. The first evidence of decomposition of the peroxides into rancid products (that is, the rancid point) can be detected by or-

ganoleptic tests about as well as by chemical tests designed to measure the aldehydes, ketones, or acids formed in the decomposition. It has been shown, however, that under controlled conditions of air oxidation at moderate temperatures the first indications of organoleptic rancidity usually can be detected at a certain level of peroxide formation. Therefore, in determining stability of fats, it has become common practice to employ a peroxide value established by organoleptic tests as an end-point of the induction period. The peroxide level used as an end-point varies with different types of fats, possibly owing partly to differences in fatty acid composition, although it has been shown also that certain antioxidants influence the peroxide level at which organoleptic rancidity may be detected.

Stability

The stability of fats is defined as their resistance to oxidative rancidity and may be expressed as the time required under specified conditions for the development of rancid odor or flavor. Under conditions of commercial storage and merchandising, this time is often too long for practical testing purposes. Therefore, reproducible conditions of accelerated aging were devised, and these have become known as accelerated stability tests. The familiar Swift stability test, oxygen absorption, and oven incubation tests are examples. One fault common to all these accelerated stability tests is that they are highly empirical and the stability values obtained by the different methods are not sufficiently correlated to permit general use of a factor for inter-conversion of values. Nor can storage or shelf life generally be accurately predicted from the results of accelerated tests. Despite these inadequacies, however, the rapid tests serve as a valuable guide in improving plant processes, in evaluating antioxidants, and in maintaining standards of quality.

Role of Antioxidants

Some means of visualizing the mechanism of atmospheric oxidation of fats is essential for better understanding of how such oxidation may be accelerated or retarded. The theory of chain reactions, postulated by Bodenstein (2) and later by Christiansen (4) furnishes a reasonable hypothesis. The first step in the oxidation involves the union of a molecule of oxygen with one of fat, after either molecule has acquired sufficient energy from its surroundings to react. The activated peroxide formed transfers its energy to one or more nearby molecules of fat, which then also become capable of reacting with oxygen. In this way, a series of reaction chains are initiated, which continue to complete oxidation of the fat or until equilibrium conditions are reached, unless the chain is interfered with by the action of a substance capable of absorbing the energy of an activated molecule. The steps in the primary oxidation

may be represented as follows, where F = fat, FO_2 = peroxide, and * = activated molecule.

1. $\text{F} + \text{Energy} \longrightarrow \text{F}^*$; $\text{O}_2 + \text{Energy} \longrightarrow \text{O}_2^*$
2. $\text{F}^* + \text{O}_2 \longrightarrow \text{FO}_2^*$; $\text{F} + \text{O}_2^* \longrightarrow \text{FO}_2^*$
3. $\text{FO}_2^* + \text{F} \longrightarrow \text{FO}_2 + \text{F}^*$
4. $\text{F}^* + \text{O}_2 \longrightarrow \text{FO}_2^*$, etc.

If antioxidant (A) is present, it is presumed to interfere with the reaction chains by one or more of the following suggested steps:

5. $\text{A} + \text{F}^* \longrightarrow \text{A}^* + \text{F}$; $\text{A}^* + \text{O}_2 \longrightarrow \text{AO}_2$
6. $\text{A} + \text{O}_2^* \longrightarrow \text{AO}_2$
7. $\text{A} + \text{FO}_2^* \longrightarrow \text{A}^* + \text{FO}_2$
8. $\text{A}^* + \text{FO}_2^* \longrightarrow \text{AO}^* + \text{FO}^* \longrightarrow \text{A} + \text{F} + \text{O}_2$
9. $\text{AO}^* + \text{F} \longrightarrow \text{A} + \text{FO}^*$

It is clear from consideration of Steps 1 to 3 that the absorption of heat or light energy would increase the number of activated molecules and the number of reaction chains. Certain metallic salts accelerate the oxidation, possibly because they increase the efficiency of energy transfer from one molecule to another.

If Steps 5 to 7 represent the role of the antioxidant in breaking the reaction chain, the antioxidant must eventually be oxidized or destroyed, unless some further mechanism of regeneration is involved. Experimental evidence has shown that, at least in some cases, the antioxidant is destroyed during the induction period of the fat. Golumbic (8) found that a rapid formation of peroxides in a fat substrate characteristic of the end of the induction period took place only after all the α -tocopherol originally present was oxidized. Similarly, Filer, *et al.* (6) found that gallic acid was oxidized or destroyed during the induction period of an oxidizing fat substrate.

In support of a mechanism of regeneration of the antioxidant, as suggested by Steps 8 and 9, Golumbic (7) found that phosphoric acid added to a fat substrate containing benzoquinone causes some formation of hydroquinone, thus suggesting that antioxidants of the hydroquinone type in an oxidizing fat substrate reach an equilibrium condition with its quinone ($\text{hydroquinone} \rightleftharpoons \text{quinone}$), which is shifted to the left by phosphoric acid.

It is inadequate to say that an antioxidant is any substance that will retard or decrease the rate of oxidation, because in special cases an agent may retard the oxidation by deactivating or removing a pro-oxidant such as a metallic salt. Furthermore, a large number of acidic compounds, among which are ascorbic, citric, tartaric, galacturonic, and phosphoric acids, bring about a marked enhancement of the stability

of fats containing phenolic or hydroquinone antioxidants, whereas they are ineffective in pure fatty acid ester substrates devoid of phenolic antioxidants. It is improbable that any single proposed mechanism would explain the role of all synergists. The suggested explanation (11) of the synergistic action of ascorbic acid with phenolic inhibitors is that the phenolic inhibitor donates hydrogen to a fat peroxide, and thereby becomes a phenoxyl radical. The phenoxyl radical readily accepts hydrogen donated by ascorbic acid and is converted back to the phenol. This process may continue until all the ascorbic acid is oxidized. Even some of the intermediate oxidation products of ascorbic acid may also furnish hydrogen. Proper combination of synergist with phenolic inhibitors may afford an economical means of stabilization.

From the foregoing, it may be said that an effective antioxidant must be capable of being oxidized in the medium and under the conditions of the oxidizing substrate. The concept of activated molecules and reaction chain mechanism of oxidation affords a reasonable basis for explaining the oxidation-retarding effect of traces of antioxidants in fats.

Practical Considerations in the Use of Antioxidants

For use in foods, an ideal antioxidant should possess the following qualifications in addition to effective inhibitory action (9, 15):

No harmful physiological effect even in quantities considerably greater than those likely to be used and even when ingested over long periods of time.

At least sufficient solubility in fats to facilitate its use; greater solubility will usually be advantageous.

Impart no objectionable odor, color, or flavor even after storage.

Be stable to whatever processing is necessary after it is incorporated in the fat.

Protective action should carry over into baked goods.

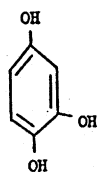
Be economical and available in quantity.

A number of substances have been made permissive for use in lard as preservatives, with provisions governing the concentration and label declarations. These substances are gum guaiac, lecithin, tocopherol concentrate, nordihydroguaiaretic acid, and citric acid. Combinations of nordihydroguaiaretic acid with citric acid and with phosphoric acid also have recently been made permissive.

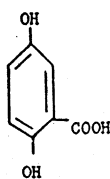
Antioxidants that have been publicized the most for possible use in commercial shortenings and edible fats have at least one hydroxyl attached to a benzene nucleus. As a rule, compounds having two hydroxyls in ortho- or para- relation on a benzene nucleus are the most effective, whereas those with meta-hydroxyls are relatively poor. Typical examples of some of these phenolic compounds are the following:



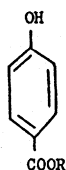
HYDROQUINONE
(BENZOQUINOL)



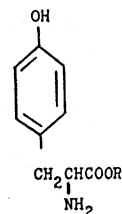
HYDROXY-
HYDROQUINONE



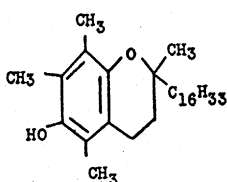
GENTISIC
ACID



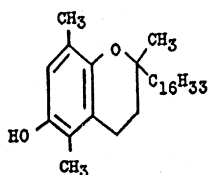
P-HYDROXY-
BENZOIC ACID
AND ESTERS



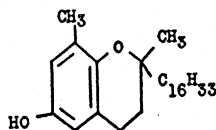
TYROSINE AND
ESTERS



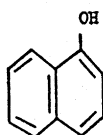
α -TOCOPHEROL



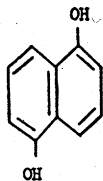
β -TOCOPHEROL



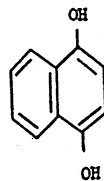
γ -TOCOPHEROL



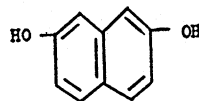
α -NAPHTHOL



1,5-DIHYDROXY-
NAPHTHALENE



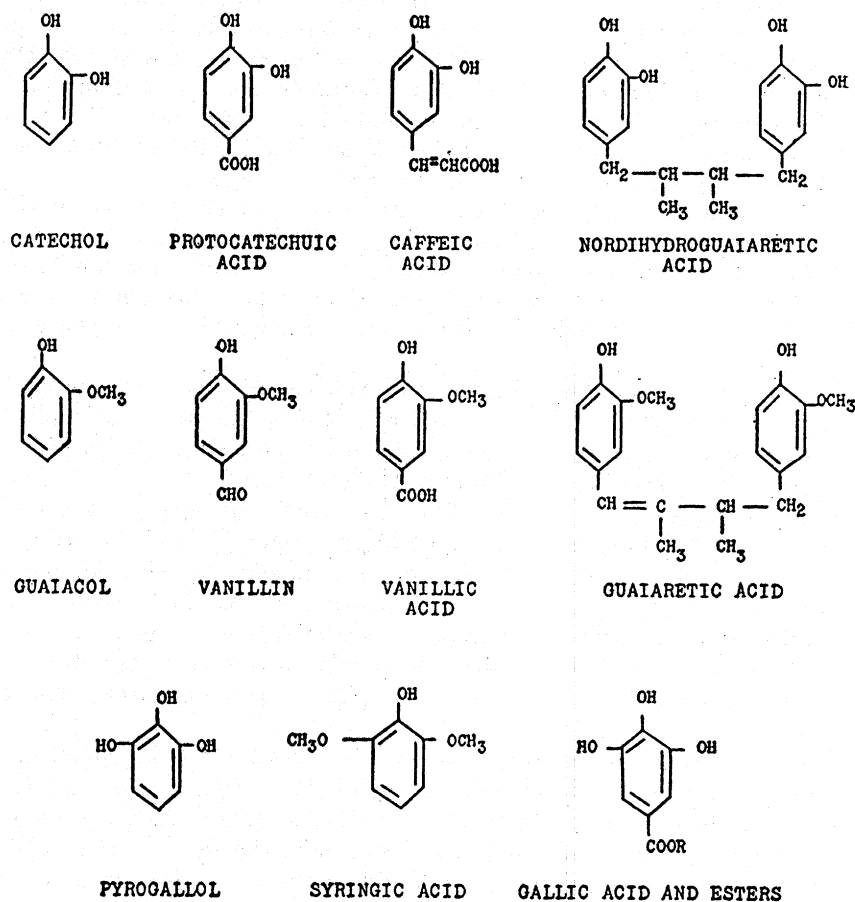
1,4-DIHYDROXY-
NAPHTHALENE



2,7-DIHYDROXY-
NAPHTHALENE

Of the compounds having but one hydroxyl attached to a benzene nucleus, α -naphthol and 1,5-dihydroxynaphthalene are probably the most effective, whereas β -naphthol, and 2,7-dihydroxynaphthalene have little or no antioxidant activity. The rest have moderate inhibitory power.

Of those having two or more hydroxyls attached to a benzene nucleus, hydroquinone, hydroxyhydroquinone, catechol, nordihydroguaiaretic acid, pyrogallol, and gallic acid (and esters) are the most effective. Strangely, 1,4-dihydroxynaphthalene has essentially no antioxidant activity. Further substitution in the nucleus generally reduces the anti-oxygenic activity; for example, protocatechuic acid is less effective than catechol. Gallic acid is less effective than pyrogallol, although still a powerful antioxidant. Nordihydroguaiaretic acid may be an exception.



in that, being a substituted catechol, it is somewhat more effective than catechol. Esterification or alkylation of one of the hydroxyls of catechol or hydroquinone, or of two of the hydroxyls of pyrogallol, greatly reduces antioxidant activity. Guaiacol, guaiaretic acid, and syringic acid may be cited as examples.

A serious fault common to many of the polyphenols cited is that they are not readily soluble in fats and oils. Compounds such as protocatechuic acid, caffeic acid, gentisic acid, and gallic acid can be converted to easily soluble compounds by esterification with aliphatic alcohols, preferably above 8 C-atoms in chain length. Owing to its greater inhibitory power, gallic acid is probably the most promising of the hydroxy derivatives of benzoic acid cited. The lower alcohol esters—methyl, ethyl, propyl, and butyl esters of gallic acid—are easily pre-

pared in good yields by the direct action of the acid and alcohol in the presence of HCL or H_2SO_4 . Similar technique with the higher alcohols resulted in very poor yields of esters. It was possible, however, to prepare the higher esters in good yields by an indirect procedure (13). More recent work (unpublished) in this laboratory has resulted in further simplification and improvement in the method of synthesis. Evaluation of the antioxidant properties of these higher alkyl gallates is under way. Preliminary results of the evaluation are encouraging.

A comparison of the relative antioxidant activity of some of these proposed compounds in a good quality lard substrate is given in Tables II and III. It should be borne in mind, of course, that these results were obtained under accelerated conditions of aging and may not show close correlation with shelf life or with results obtained under storage conditions.

Other interesting nonphenolic antioxidants have also been proposed, such as thio-ethers and substituted thio-ethers, thiourea, phospholipids, and a number of the amino acids. Thiourea and amino acids function best in substrates containing appreciable moisture.

A few general observations may be mentioned regarding the use of synergists. Organic acids containing hydroxyl groups, such as citric, tartaric and galacturonic acids, seem to be more effective with polyphenols than with tocopherol, whereas phosphoric acid, lecithin, ascorbic acid, and fatty acid esters of ascorbic acid are effective synergists for mono- and polyphenols. These acidic compounds are metal deactivators, and this may account in part or in some instances for the apparent beneficial effect.

It is not justifiable to use numerical values for a strict quantitative comparison of the antioxygenic powers of the various compounds. However, protection factors have been used in a limited sense to indicate comparative stabilizing power. This factor is the ratio of the stability of the substrate containing the antioxidant to that of the substrate. The protection factor for a given antioxidant may vary greatly, depending on the fatty acid composition of the substrate and the amount and character of minor constituents present (whether antioxygenic or pro-oxygenic), and also in some cases depending on the stability test employed. Therefore, comparisons should be qualified accordingly.

Much more work of a practical nature is required before any conclusions can be drawn as to the suitability of the various compounds mentioned (other than those already approved) for edible products. It should be emphasized, however, that even the best antioxidant should not be considered a cure-all for rancidity. Attention should also be given to factors important in deriving the maximum benefit from approved antioxidants.

TABLE II

STABILIZING EFFECT OF ANTIOXIDANTS IN LARD AS DETERMINED BY THE ACTIVE OXYGEN METHOD AND BY THE OXYGEN ABSORPTION METHOD
(BARCROFT-WARBURG APPARATUS) (16)

Antioxidants added, %	STABILITY (HOURS)			PROTECTION FACTORS		
	A.O.M. (moist air) 98.5°	A.O.M. (dry air) 98.5°	O ₂ -Abs. (B-W) 100°	A.O.M. (moist air) 98.5°	A.O.M. (dry air) 98.5°	O ₂ -Abs. (B-W) 100°
Control (steam-rendered lard-C)	7	6	3.0	1	1	1
+ .01 α -tocopherol	20	19	8.6	2.9	3.2	2.9
+ .01 β -tocopherol	24	21	11.0	3.4	3.5	3.7
+ .01 γ -tocopherol	28	30	14.5	4.0	5.0	4.8
+ 6.4 ¹ refined corn oil	20	20	12.3	2.9	3.3	4.1
+ .01 α -tocopherol + .01 citric acid	21	21	11.0	3.0	3.5	3.7
+ .005 propyl gallate	40	42	20.1	5.7	7.0	6.7
+ .005 propyl gallate + .01 citric acid	50	50	24.8	7.1	8.3	8.3
+ .005 NDGA ²	58	50	26.9	8.3	8.3	9.0
+ .005 NDGA + .01 citric acid	67	62	32.8	9.6	10.3	10.9
+ .01 catechol	44	43	28.9	6.3	7.2	9.6
+ .01 catechol + .01 citric acid	48	48	43.2	6.9	8.0	14.4
+ .005 benzylhydroquinone	43	44	11.0	6.1	7.3	3.7
+ .005 benzylhydroquinone + .01 citric acid	50	50	14.1	7.1	8.3	4.7

¹Equivalent to .01% tocopherol.

²Nordihydroguaiaric acid.

TABLE III
STABILIZING EFFECT OF ANTIOXIDANTS IN LARD AS DETERMINED
BY THE ACTIVE OXYGEN METHOD (14)

Antioxidants added, %	STABILITY		PROTECTION FACTORS	
	Moist Air hrs.	Dry Air hrs.	Moist Air	Dry Air
Control (steam-rendered lard)	8	8
+ 0.1 gum guaiac	24	24	3.0	3.0
+ 0.05 mixed tocopherols	18	18	2.3	2.3
+ 0.01 nordihydroguaiaretic acid	86	89	10.8	11.1
+ 0.05 citric acid	11	10	1.4	1.3
+ 0.1 d-isoascorbyl palmitate	17	12	2.1	1.5
+ 0.1 l-ascorbyl palmitate	25	17	3.1	2.1
+ 0.1 l-ascorbic acid	18	13	2.3	1.6
+ 0.1 lecithin	14	10	1.8	1.3
+ 0.05 triethanolamine	17	9	2.1	1.1
+ 0.05 thiourea	27	16	3.4	2.0

Importance of Quality of Substrate

The quality of the fat to which antioxidants are added is an important factor in determining how much increase in stability will be achieved. The data in Table IV show, for example, that antioxidants impart much greater increase in stability to lard of good initial stability than to lard of poor stability, thus stressing the need for greater care in processing the raw materials.

TABLE IV
STABILIZING EFFECT OF ANTIOXIDANTS ADDED TO POOR- AND GOOD-QUALITY LARD
AS DETERMINED BY THE ACTIVE OXYGEN METHOD

Antioxidants added, %	STABILITY		INCREASE IN STABILITY	
	Poor Quality hours	Good Quality hours	Poor Quality hours	Good Quality hours
None (control)	2	8
+ .0025 NDGA ¹	6	26	4	18
+ .005 NDGA	12	32	10	24
+ .01 NDGA	14	56	12	48
+ .005 NDGA + .02 C.A. ²	43	58	41	50
+ .01 tocopherol	11	20	9	12
+ .01 toc ³ + .02 d-IP ⁴	16	37	14	29
None (control)	1	9
+ .01 tocopherol	10	26	9	17
+ .06 lecithin	3.5	14	1.5	5

¹Nordihydroguaiaretic acid
²Citric acid

³Tocopherol
⁴d-Isoascorbyl palmitate

Importance of Amount and Type of Unsaturated Fat Components

It has been shown (Table I) that the ease of oxidation of fats is not merely a function of the iodine number but is even more directly related to the content and type of polyunsaturated constituents. Antioxidants then might reasonably be expected to impart greater increase in stability to fats containing smaller proportions of polyunsaturated constituents. Some indication that this is generally true may be gained from the results shown in Table V. The increase in stability resulting from the addition of antioxidants to methyl oleate is considerably

TABLE V
EFFECT OF ANTIOXIDANTS ON THE OXYGEN-ABSORPTION OF
METHYL ESTERS OF FATTY ACIDS (BARCROFT-WARBURG APPARATUS, 100° C) (18)

Antioxidants added (0.01 percent)	STABILITY ¹	
	Me Linoleate hours	Me Oleate hours
None	0.2	2.0
+ α -tocopherol	0.7	8.5
+ α -toc ² + lec ³ + d-IP ⁴	1.3	36.0
+ NDGA ⁵	2.4	43.5
+ NDGA + C.A. ⁶	3.5	135.0
+ Propyl gallate	1.6	34.2
+ Propyl gallate + C.A.	2.6	101.0
+ Benzyl hydroquinone	1.4	13.0
+ Benzyl hydroquinone + C.A.	2.1	22.5

¹Time required to absorb 1 gm. of oxygen per kg.

²Tocopherol

³Lecithin

⁴d-Isoascorbyl palmitate

⁵Nordihydroguaiaretic acid

⁶Citric acid

greater than that produced when it is added to methyl linoleate. These results also explain the great increase in stability of hydrogenated vegetable shortenings over that of the original oil. The natural antioxidants present exert proportionately much greater effect after the polyunsaturates are decreased by hydrogenation.

Oxidative Deterioration in Cereal Products

Important factors that influence the stability of cereal products, such as crackers and biscuits, have been thoroughly discussed in a number of published articles (3, 9, 10, 12, 19, 20, 21), several of which are fairly recent. Although most of these factors are now common knowledge, perhaps a brief outline of them will serve as emphasis. Investigation of these influencing factors was prompted in many instances by the general observation that no direct relation existed between the stability of the cracker or baked product and the stability of the shortening used. In many instances there seemed to be little or no relation between the

two, although on the average, crackers of better keeping quality were obtained with the more stable shortenings.

Factors Influencing the Stability of Crackers

1. According to Bohn and Olson (3), the fatty acid composition of the shortening is the most important factor in the stability of crackers. Shortening high in polyunsaturated acids such as linoleic acid results in crackers of low stability. In a general way, the data given in Table V support this statement.

2. Antioxidants, either inherent or added, may be lost to an appreciable extent during processing or baking. Some antioxidants, more volatile and labile than others, suffer greater loss, and in these cases greater discrepancy between the stability of the shortening and cracker results. Gum guaiac (9) and nordihydroguaiaretic acid (9, 10) show a fair degree of carry-over of antioxygenic activity into baked crackers, whereas tocopherols, propyl gallate, and esters of ascorbic acids are relatively poor in this respect. Nordihydroguaiaretic acid (10) is more effective in pie crust than in crackers. We are now investigating the importance of solubility of antioxidants in fats in relation to the carry-over of their oxidation inhibitory power into baked products.

3. Certain pro-oxidants, such as fat peroxides, are destroyed during the processing of the cracker (20). This observation has been confirmed in our laboratory, where it was further found that merely mixing the ingredients for cracker dough reduced the peroxide value of the lard from 7.9 to 2.8. After fermentation, the peroxide value (of the extracted fat) was reduced to zero and remained there even after 3-, 6-, and 9-minute baking periods, and also after 4- and 7-minute crisping periods. The stability (oven test at 145° F.) of the fat extracted at the various stages increased from 4 hours for the original lard to about 50 hours after the dough was rolled and cut. The stability of the fat extracted after 6 minutes' baking further increased to about 120 hours and remained about the same from there on through the crisping. Apparently, the flour or combination of flour and other ingredients has the power of reducing fat peroxides. The fat then becomes more nearly like its original fresh condition and is further stabilized by natural antioxygens of the wheat oil, tocopherols. These observations form a reasonable explanation for the findings that often crackers of comparable stability can be made with either poor- or good-keeping lard.

4. Variations in time and temperature of baking no doubt cause significant variations in cracker stability.

5. Traces of metallic contamination in the dough, possibly caused by the equipment used in mixing, rolling, cutting, and baking operations, are powerful pro-oxidants. The flours also may have variable metal content.

6. The shelf life of commercial baked products may be greatly influenced by the character of the package, as discussed by Triebold (21) and Maveety (12).

It is apparent from the foregoing discussion that the practical solution of the problem of rancidity cannot be achieved by using antioxidants in a superficial and desultory manner, but will be achieved only by the most rigid and careful application of the principles of good processing technology in combination with the judicious use of antioxidants.

Literature Cited

1. Bergström, S.
1945 Autoxidation of linoleic acid. *Nature* 156: 717-718.
2. Bodenstein, M.
1913 Eine Theorie der photochemischen Reaktionsgeschwindigkeiten. *Z. physikal Chemie*. 85: 329-397.
3. Bohn, R. M. and Olson, R. S.
1934 Some factors affecting rancidity. *Oil and Soap* 11: 210-220.
4. Christiansen, J. A. and Kramers, H. A.
1923 Über die Geschwindigkeit Chemischer Reaktionen. *Z. physikal Chemie*. 104: 451-471.
5. Farmer, E. H., Koch, H. P. and Sutton, D. A.
1943 The course of autoxidation reactions in polyisoprenes and allied compounds. Part VII. Rearrangement of double bonds during autoxidation. *J. Chem. Soc.* 541-547.
6. Filer, L. J., Jr., Mattil, K. F., and Longenecker, H. E.
1944 Antioxidant losses during the induction period of fat oxidation. *Oil and Soap*. 21: 289-292.
7. Golumbic, C.
1942 The antioxygenic action of phosphoric acid in association with tocopherols and hydroquinones. *Oil and Soap*. 19: 181-182.
8. 1943 The autoxidative behavior of vegetable and animal fats. *Oil and Soap* 20: 105-107.
9. Higgins, J. W., and Black, H. C.
1944 A preliminary comparison of the stabilizing effect of several recently proposed antioxidants for edible fats and oils. *Oil and Soap*. 21: 277-279.
10. Lundberg, W. O., Halvorson, H. O., and Burr, G. O.
1944 The antioxidant properties of nordihydroguaiaretic acid. *Oil and Soap*. 21: 33-35.
11. Mattill, H. A.
1945 Antioxidants and synergists. *Oil and Soap*. 22: 1-3.
12. Maveety, D. J.
1946 Correlation of keeping properties of shortenings with keeping quality of biscuits. *Oil and Soap*. 23: 25-27.
13. Morris, S. G., and Riemenschneider, R. W.
1946 The higher fatty alcohol esters of gallic acid. *J. Am. Chem. Soc.* 68: 500-501.
14. Nagy, J. J., Beadle, B. W., and Kraybill, H. R.
1945 Use of dried air in the active oxygen method of determining relative stabilities of fats. *Oil and Soap*. 22: 123-124.
15. Riemenschneider, R. W., and Ault, W. C.
1944 How to evaluate and improve the stability of fatty foods. *Food. Ind.* 16: 892-894; 936-939.
16. ———, Luddy, F. E., Herb, S. F., and Turer, J.
1945 Stability values obtained by different rapid methods as a means of evaluating antioxidants for fats and oils. *Oil and Soap* 22: 174-177.

17. Staudinger, H.
1925 Ser. — Über Autoxidation Organischer Verbindungen. Part III. Über Autoxidation des *asymm.* dichenyl-äthylens. Ber. 58B:1075-1079.
18. Stirton, A. J., Turer, J., and Riemenschneider, R. W.
1945 Oxygen absorption of methyl esters of fat acids, and the effect of antioxidants. Oil and Soap. 22:81-83.
19. Triebold, H. O.
1931 Rancidity. Cereal Chem. 8:518-532.
20. ———, Webb, R. E., and Rudy, W. J.
1933 A chemical study of rancidity III. Some recent developments in the study of oxidative rancidity of special interest to the cereal industry. Cereal Chem 10:263-276.
21. ———,
1945 Oxidative deterioration of fats in cereal products. Oil and Soap. 22:334-336